

Rolling up of graphite sheet: Energetics of shell formation

Slava V. Rotkin, Robert A. Suris

*Ioffe Physico-Technical Institute of Russian Academy of Sciences,
26 Politekhnicheskaya St., St.Petersburg 194021, Russia*

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The energetics of transformation of a planar fragment of a graphite monolayer into a spherical cluster is studied. The path considered is that a flat cluster rolls up into a segment of a spherical shell. The energy landscape of the process is presented. A simple model, formerly invented for calculating the carbon nanocluster formation energy, is used to evaluate the energies of intermediate states. Although the spherical-shell closed cluster has the lowest energy, curving of a plane fragment into a segment has an energy barrier. The barrier height goes to zero for clusters with the number of atoms greater than some N_{th} , for which the cluster size is found analytically.

The aim of the work is to study the energetics of formation of curved carbon nanoscale clusters (CNC). If the synthesis conditions more or less correspond to equilibrium, the energy considerations give an insight into the mechanisms of cluster formation, which explains the persistent theoretical interest in the CNC energetics [1–4]. This led us to propose a new phenomenological model in Refs. [5,6]. In the frame of the model, only three parameters allow estimating the formation energies for a variety of clusters within unified analytical approach. When these parameters are furnished by quantum-chemical calculations or extracted from experiment, a number of general laws related to the cluster stability is deduced.

In the paper, we consider clusters which can serve as intermediates for rolling of a flat fragment of a graphite monolayer into a closed sphere. Tube formation will be discussed elsewhere [7,8]

The continual approximation is supposed to be valid for a curved graphite-like surface. The model assumes that the carbon bonds are the same for all atoms in any cluster (excepting bonds belonging to a pentagonal defect of the pristine honeycomb lattice of 2D graphite). We argue that, at least for the large cluster [9], the continual approach works well. We extrapolate the results of the continual approach and apply the model to an interesting case of comparatively small clusters with the number of atoms, N , of about a hundred. We state that, despite the simplification, the model adequately estimates the CNC formation energy for a tube, sphere, and capsule [6,10].

The paper proceeds as follows: Section I deals with the fundamentals of our model, illustrated by examples of a carbon nanotube and spherical cluster (a detailed description of our approach was presented in Refs. [5,11,12]). In Section II we discuss the energetics of a possible mechanism by which a spheroidal cluster can be formed by rolling-up of a piece of a graphite-like plane. Finally, a summary is given.

I. ENERGY OF CURVED GRAPHITE SURFACE

Three phenomenological parameters were used [11,12] to calculate the additional energy of CNC formation, as compared with the known specific energy of an infinite graphite sheet (graphene). The energy of any carbon cluster with a curved surface is decomposed into additive terms. Each term is given by some characteristic energy (the model parameter) multiplied by a number depending solely on the cluster geometry. This essential simplification of the calculation is based on natural reasoning. There are 3 sources bringing at least 3 parameters into the energy (excepting the "zero energy" of an atom belonging to an infinite graphite sheet; this term is excluded from further expressions). The first additional term comes from dangling bonds. The corresponding energy parameter, E_b , is the dangling bond energy. An extra energy due to a change of the degree of a hybridisation of an electron orbit on the curved surface is described using the second parameter, E_c . The last parameter, E_5 , is the total energy of twelve pentagonal rings. This parameter reflects that an electron belonging to the pentagon must have energy different from that in a graphite-like hexagon. Hence, it partly takes into account non-equivalent bonds. Note that this is a topologically determined donation to the total energy of any closed cluster [13].

In general, the curvature of a surface is a function of a point. The curvature is constant and equal to $3/R^2$ for a sphere of radius R , and $9/8R^2$ for a tube of the same radius. For the sake of clarity, we consider here only the surface with constant curvature. One easily obtains the formation energy of an infinite carbon tube. The specific energy of dangling bonds is negligible since it goes to zero with the tube size going to infinity. A tube has no pentagon, because a cylinder is topologically equivalent to a plane. Hence, the energy has only one term, the "curvature energy" $E = E_c 9N/8R^2$, where N is the number of atoms and R is the dimensionless tube radius. Henceforth, all lengths will be measured in bond lengths ($b \simeq 1.4\text{\AA}$ not supposed to vary according to the model). We compared the tube energy

with the relevant results of other computations [3]. This gave the first parameter of the model: $E_c \simeq 0.9$ eV (see also [5,11]).

Most likely, the energy of a dangling bond in CNC does not differ too much from the value for graphite, and therefore, we took $E_b = 2.36$ eV. The total energy associated with the dangling bonds is proportional to the cluster perimeter length (length of the open boundary of the CNC lattice) multiplied by the density of dangling bonds along the perimeter, which in turn depends on the local geometry. One can imagine, for example, a finite tube as a parallelogram, carved from hexagonal graphene, which has its opposite sides glued [3,14]. This parallelogram has a variable number of sites on the open perimeter ζ (dangling bond density), depending on its orientation relative to the lattice vector. None the less the density varies in a narrow region. If we take the geometrical factor in ζ to be unity for the "zigzag" tube, then it becomes $2/\sqrt{3}$ for the "armchair" tube; one can easily calculate ζ for the bond density of a specific tube lying between these extreme examples.

It was shown in our previous papers [5,11,12,15], that there occurs **competition** in the formation energy of a finite tube between two terms with E_c and E_b (the energy associated with dangling bonds can not be neglected for a tube of finite length). The tube energy reads as: $E(N, R) = E_c 9N/8R^2 + E_b 4\pi\zeta R/\sqrt{3}$. It is advisable to make the total perimeter $4\pi R$ shorter in order to diminish the number of dangling bonds. The radius decrease costs an extra total energy owing to stronger curvature. We called the cluster having the minimal energy at a certain number of atoms "an optimal cluster". The optimal cluster is the configuration governed by energy consideration at any fixed N . (The nanotube energetics and the tube formation road from a flat graphene were discussed in details in Ref. [8]). Thus, we constructed a phenomenological approach and predicted the optimal cluster shape, based on the energetics of any nanotube without performing a quantum-chemical calculation each time.

The third parameter of the model was determined by fitting the formation energy of a spherical cluster to the experimental value for C_{60} . The total energy of a sphere consists of two components [11]. The first constant component is the energy of 12 pentagons. The sphere energy also includes the total curvature energy which is independent of the radius in this case (because the number of atoms being proportional to squared curvature, $1/R^2$). The second component is a correction excluding pentagonal bonds from the total count of curved bonds. Therefore, the energy is as follows:

$$E_{\text{sph}} = \left(E_5 + \frac{16\pi E_c}{\sqrt{3}} \right) - \frac{N_s}{N} E_c \quad (1)$$

where we introduce a characteristic number $N_s = 2 \times 60 \times 16\pi/3\sqrt{3} \simeq 1161$. The number N_s includes the number of bonds belonging to the pentagonal rings in the fullerene (cf. also [11]) and the (dimensionless) curvature of the surface times the (dimensionless) area of the sphere covered by hexagons. We took the experimental value of C_{60} formation energy from Ref. [16] and fitted our last parameter $E_5 \simeq 17.7$ eV, which takes into account all 12 pentagons of the spheroidal closed cluster. The sphere energy evidently remains positive (for the given model parameters $E_c=0.9$ eV and E_5) for the smallest spherical cluster considered here, C_{60} . Then, comparing the experimental formation energy of C_{70} with our calculation, we find that the difference is about 1% and all three parameters are self-consistent.

II. HOW SPHERE IS ROLLED UP

A sphere has the minimal curvature energy between closed nanoclusters of any definite number of atoms, $N = \text{const}$. It seems interesting to compare the energies of **closed clusters** with the energy of **an open fragment** having dangling bonds. For an open CNC, the shorter the perimeter (number of dangling bonds), the stronger the curvature. The decreasing energy of dangling bonds makes favourable a small rolled-up cluster with a shorter perimeter. The curvature energy demands that the CNC be extended and flat. As a result of the energy competition, the system decreases its total energy via elimination of dangling bonds owing to the fact that the infinitely large sphere is a configuration resulting in the global minimum of the total CNC energy [11].

We consider below a sphere (of area S_o) with a round hole of angular size Ω varying from 0 to 4π , from the sphere to the round piece of the plane (see Fig.1). This means that we choose a flat CNC with **the minimal perimeter** (round) and a closed CNC with **the minimal curvature** (sphere) at fixed area or number of atoms. We name an intermediate cluster "an open sphere". The curvature energy decreases with the open sphere surface area as $(1 - \Omega/4\pi)S_o$. This can be seen from the expression for the number of atoms in an ideal graphene sphere with a round hole: $N = (1 - \Omega/4\pi) 16\pi R^2/3\sqrt{3}$. It is also natural to feather out the dependence of the topological energy $E_5(\Omega)$ in the hole size Ω (actually varying stepwise, each step correspondes to creating a pentagonal defect) and to substitute a linear dependence. Instead of choosing a specific way to create a defect and to place it in the cluster

lattice, the simplest uniform distribution of pentagons over the open sphere surface is used here [17]. This is nearly equivalent to placing pentagons as far apart as possible. The kinetics of the process [18] is not touched on in this paper, as well as the pentagon–pentagon distance optimised elsewhere [7].

In terms of the independent variables R and Ω (or N and Ω alternatively) the energy of the open sphere reads as:

$$\begin{aligned} E(N, \Omega) &= \left(1 - \frac{\Omega}{4\pi}\right) \left(E_5 + E_c \left[\frac{16\pi}{\sqrt{3}} - \frac{120}{R^2}\right]\right) + \frac{4\pi R E_b}{\sqrt{3}\zeta} \sqrt{\frac{\Omega}{4\pi}} \sqrt{1 - \frac{\Omega}{4\pi}} = \\ &= \left(1 - \frac{\Omega}{4\pi}\right) \left[E_5 + \frac{16\pi E_c}{\sqrt{3}} - E_c \frac{N_s}{N} \left(1 - \frac{\Omega}{4\pi}\right)\right] + 2 \left[E_5 + \frac{16\pi E_c}{\sqrt{3}}\right] \frac{1}{\sqrt{N_{\text{th}}}} \sqrt{\frac{N\Omega}{4\pi}} \end{aligned} \quad (2)$$

where ζ is a geometrical multiplier of about unity [19], and we introduce N_{th} , a "threshold" size of planar cluster, given by: $\frac{\sqrt{\pi\sqrt{3}} E_b}{\zeta 2[E_5 + \frac{16\pi}{\sqrt{3}} E_c]} = \sqrt{N_{\text{th}}^{-1}}$. Its meaning is discussed just below. The first term in Eq.(2) is the energy of an incomplete sphere. The second is the dangling bond energy. Of course, the accuracy of the model is poorer for small N and strong curvature [20]. As it is seen from Figure 2, the energy of the open sphere with hole size of neither 0 nor 4π has a maximum at fixed number of atoms when $N \leq N_{\text{th}} \simeq 254$. Partial differentiation of Eq.(2) with respect to Ω (at fixed N) gives an analytical expression for the size of the open sphere with the maximal energy. The function is given (with high accuracy for $N > 100$) by:

$$\Omega_B \simeq 4\pi \left(1 - \left(1 - \frac{N}{N_{\text{th}}}\right) \frac{N}{N + 4N_s / \left[\frac{E_5}{E_c} + \frac{16\pi}{\sqrt{3}}\right]}\right). \quad (3)$$

The line given by Eq.(3) intersects the abscissa axis at $\Omega = 4\pi$ and N_{th} , named "the threshold flat cluster" in the following sense.

Let us consider a set of CNCs with $N < N_{\text{th}}$ and $4\pi < \Omega < 0$: the energy of a cluster with $N = \text{const}$ grows in moving away from both extremities of this interval and has a maximum at $\Omega = \Omega_B$. That is, going from $\Omega = 4\pi$ to $\Omega = 0$ (where the minimum of the energy occurs at fixed N), we pass through a barrier of height $\delta E(N) = E(N, \Omega_B) - E(N, 4\pi)$ decreasing with N and tending to zero at N_{th} . Therefore, as follows from energy consideration solely, planar clusters with $N \geq N_{\text{th}}$ can be rolled up without any barrier. Below N_{th} , the flat CNC is metastable to the rolling–up. Suppose we have initially some distribution of planar graphite fragments $f(N)$ (which is consistent with the two–step–model of carbon cluster formation proposed in [21] where nucleation and growth processes were separated). It is energetically favourable to increase the number of atoms, but this process depends on availability of the building material (carbon atom concentration). One can suppose that in the second step of synthesis the only conformation is possible between different clusters (even through some exchange of carbons).

We consider below that the change in number of atoms is suppressed. Suppose that the most energetically favourable process is rolling–up of a flat CNC into a sphere [22]. Then clusters with $N > N_{\text{th}}$ are rolled–up for energetical reason. At some finite temperature T , the probability to roll up a smaller cluster is exponentially small: $W \propto \exp(-\delta E/T)$, where δE is the barrier height (shown in Figure 2) depending on N and Ω . This is the difference between the energy of the given flat cluster and that of a "barrier" cluster with the same number of atoms.

As a result of rolling–up, the initial size distribution of planar clusters is changed. We discussed above only a single path of conformation (rolling–up into the spherical-shell cluster). For this reason we can only speculate about the distribution of the rest of planar clusters. It has a maximum depending on temperature and characteristic number of atoms in the initial distribution $f(N)$, being determined by the conditions of two distinct synthesis regimes and, therefore, treated as independent .

In summary, we proposed a heuristic model for calculating the energy of a carbon nanocluster formation. Within the model, we use only three phenomenological parameters extracted from computer simulations and experimental data. The model allows evaluating the formation energies of various CNCs and finding the preferable cluster shape.

We compared the formation energies of the most preferable closed cluster (spherical cluster) and the most preferable flat fragment (round piece of graphene). We conclude that for energy reasons rolling–up of a flat fragment is always favourable, since the energy of a closed cluster is the lowest. We predict that a small enough flat graphite cluster can be metastable with respect to rolling into a shell. The energy barrier for rolling is calculated and shown to disappear for the clusters containing more than three hundred atoms.

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- [17] The position of pentagonal defects in the energetically optimal cluster lattice is not known exactly. The Isolated-Pentagon-Rule works for the closed clusters. Even if we suppose uniform distribution to be valid for an open cluster, a possible reconstruction of the open perimeter is to be considered. This may lead to additional tension of surface and reshaping of the cluster through pentagon migration. Also, the kinetics of pentagon diffusion seems to be non-trivial [18]. These effects are far beyond the scope of the paper and will be discussed elsewhere.
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- [20] If one extrapolates Eqs.(2) and (3) to very small clusters ($N < 60$), at least Eq.(1) fails owing to the fact that all atoms belong to the pentagons and some of the bonds become inequivalent. The strain energy has to increase with increasing $1/R^2$. Thus, the model underestimates the energy of smaller clusters. However, one can use the model for small flat and slightly curved fragments of plane with some pentagons. That is, the lower the pentagon density (the number of pentagons per CNC area, see [9] above), the better the model accuracy.
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The supposed path of spherical-shell closed cluster formation: from a flat round fragment of graphene, $\Omega = 4\pi$ (right), via open spheres with $0 < \Omega < 4\pi$ (center), to a shell, $\Omega = 0$ (left). The number of atoms is kept constant. Therefore, the linear size decreases.

The energy landscape of the process of rolling-up. The barrier height for rolling-up is shown. The energy of a flat round fragment of graphene is lower than that of an intermediate state, the open sphere, depending on hole size Ω and number of atoms N . The barrier disappears at $N > N_{\text{th}}$, as described in the text.

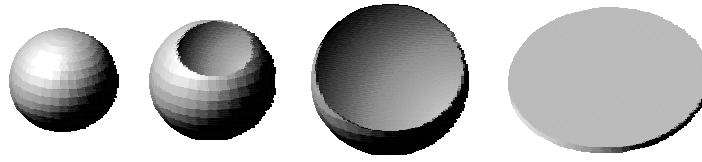


FIG. 1. The supposed path of spherical-shell closed cluster formation: from a flat round fragment of graphene, $\Omega = 4\pi$ (right), via open spheres with $0 < \Omega < 4\pi$ (center), to a shell, $\Omega = 0$ (left). The number of atoms is kept constant. Therefore, the linear size decreases.

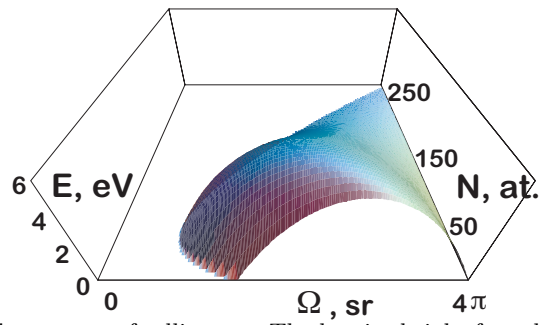


FIG. 2. The energy landscape of the process of rolling-up. The barrier height for rolling-up is shown. The energy of a flat round fragment of graphene is lower than that of an intermediate state, the open sphere, depending on hole size Ω and number of atoms N . The barrier disappears at $N > N_{\text{th}}$, as described in the text.